IONIZATION OF MOLECULES AT THE FLUID-FLUID PHASE TRANSITION IN WARM DENSE HYDROGEN

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An idea is introduced that ionization of H_2 molecules takes place at the fluid-fluid phase transition in warm dense hydrogen/deuterium with formation of molecular ions H_2^+ and H_3^+. Density functional theory with the VASP plane-wave code is used. Proton-proton pair correlation functions (PCF) g(r), conductivity and pressure are calculated. Three PCF treatment procedures are applied to reveal a nature and character of the phase transition. (1) PCF varies slowly with the density in the range of distances larger than 2Å. However, the situation changes drastically for distances smaller than 2Å. The values of the PCFs first local maxima $g(r_{max1})$ and first local minima $g(r_{min1})$ are changed dramatically in the narrow density range. To emphasize the character of g(r) changes, plots of $g(r_{max1})/ g(r_{min1})$ are obtained. Strongly pronounced jumps for T = 700, 1000, 1500 and 2500 K are clear indications of the phase transition since they take place at the same densities where small density jumps are observed. The dependence of discontinuity of ratio $g(r_{max1})/ g(r_{min1})$ on temperature gives us the estimation of critical temperature T_c~4000K which agrees with recent data of Mochalov et al.

(2) The value of r_{max1} is equal to the interatomic distance 0.74Å, in the H_2 molecule. The value of r_{min1} is close to the interatomic distances 1.06Å, and 0.92Å, in the molecular ions H_2^+ and H_3^+. Let $g_1(r)$ and $g_2(r)$ are PCF's which are the closest to the phase transition before and after it. $\Delta g(r)= g_2(r)-g_1(r)$ is close to zero for r>2Å. The function $\Delta g(r)$ has a deep minimum at r=0.74Å and a strongly pronounced maximum in the range of r from 0.92Å to 1.06Å. It means that the number of H_2 decreases and ions H_2^+ and H_3^+ appears at the phase transition.

(3) The ratio of the second maxima and minima $g(r_{max2})/ g(r_{min2})$ varies smoothly with the density. It turns out that the PCF's obtained can be modeled for r > 2Å, by the soft sphere PCF's at number densities which are equal to the total density of H_2, H_2^+ and H_3^+. The latter value remains close to the constant one at the phase transition. The repulsion “diameters” is close to the theoretical estimate. A two-step mechanism is suggested. The first stage is related to the partial ionization of H_2 molecules at the phase transition with formation of the molecular ions H_2^+. The second stage is a reaction of H_2 molecules and H_2^+ ions to form H_3^+ ions. The nature of the phase transition combines the ionization and the structure transformation. Strong ionization can be related to the Norman-Starostin plasma phase transition prediction. However, it differs from it by inherent structural changes. The transition in WDH is an exceptional case.

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